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<b>12a. DISTRIBUTION / AVAILABILITY STATEMENT</b>  Approve for Public Release: Distribution Unlimited			<b>12b. DISTRIBUTION CODE</b>	
<b>13. ABSTRACT (Maximum 200 Words)</b> Remarkable progress has been achieved in our investigations of photoinduced magnetism (PIM) in several families of molecule-based magnets during the past three years. The advancements include development of utilization of a new experimental method in studies of PIM, report of the first system with coexisting photomagnetic and spin glass behavior, proposal of a new mechanism for photomagnetic effects in Prussian blue magnets, and, discovery of the first organic-based light-modulated magnet. Based on our elaborate magnetic and PIM studies of a series of Co-Fe Prussian blue analogs, we determined a highly unconventional type of magnetic ordering and proposed the first model for PIM effects that accounts for the observed cluster glass behavior. The experimental studies included the first use of ac susceptometry in investigation of PIM. This allowed the first direct observation of light induced changes in spin dynamics. Our discovery of PIM in an organic-based magnet, $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ resulted in dramatically higher PIM operating temperature (close to nitrogen boiling temperature of 77 K) than the one characteristic for Prussian blue magnets (~20 K). Photoinduced optical studies revealed that PIM in this material is accompanied by changes in the electronic configuration as well as structural changes, entirely different than the Prussian blue magnets PIM mechanism.				
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## Final Report

Development of magnetically, optically, electronically as well as electrically modulated materials, the properties of which can be deliberately by external stimuli or by synthesis methods is of great importance for modern technology. An attractive possibility is using light to control material properties, particularly in the context of the rapidly developing field of photonics, in which light, rather than electrical current, is used in information transfer and processing. This would provide new options for the development of 'smart materials [1].' Magnetic materials with magnetic properties tunable with light may lead to a new mode of control in ubiquitous magnet-based devices. In particular, as the information technology's ever increasing need for faster information processing speeds and higher storage densities require new ways to write, erase, and read information, the possibility to manipulate information bits in a magnetic medium at microscopic (molecular) level by light beams is very attractive.

A textbook example of materials for which the magnetic properties can be changed by light irradiation are paramagnetic spin crossover complexes, in which visible light induces changes in spin configurations of individual metallic ions [2]. In these systems, however, individual elementary magnetic moments ('spins') interact very weakly and no cooperative magnetic behavior (magnetic order) is present, thus the materials have measureable, but relatively very weak magnetic signals. In 1996 a fundamentally different photoinduced effect was discovered in 'Prussian blue' magnets [3]. In these materials, which belong to the class of molecule-based magnets [4], photoinduced magnetic phenomena (photoinduced magnetism, or PIM in the text that follows) coexist with cooperative magnetic behavior, i.e., with magnetic order. This coexistence brings about a possibility for optical control of the magnetic order which leads to strong magnetic signals (even exceeding the magnetic signal before photoexcitation), and a number of novel, spectacular and readily detectable effects.

Motivated by the initial report of photoinduced effects in Prussian blue magnets we initiated the project on photoinduced magnetism aimed at detailed characterization of these materials, understanding the fundamental mechanisms of PIM, identification of new materials exhibiting enhanced PIM effect, and optimizing PIM properties for possible applications. The project built upon our nearly two decades of experience with synthesis and characterization of organic-, molecule-, and polymer-based magnets, including the introduction and characterization of several classes of organic-based magnet materials.

The progress in the studies of photoinduced magnetism we have made in the three-year initial grant period is remarkable, and includes advances in experimental methods, understanding of fundamental PIM mechanisms, and synthesis of a new light-tunable magnet.

Based on our elaborate magnetic and PIM studies of a series of Co-Fe Prussian blue analogs, we determined a highly unconventional type of magnetic ordering in this class of materials and proposed the first model for PIM effects that accounts for the observed cluster glass behavior. The experimental studies included the first use of ac susceptometry in investigation of PIM. The application of photoinduced ac susceptometry allowed for the first time the direct observation of the light induced changes in spin dynamics.

Our search for new light-tunable magnets brought about a discovery of the first such system based on organic species,  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$ . The significance of this finding lays both in its novelty and in the dramatically higher operating temperature (close to nitrogen boiling temperature of 77 K) then the one characteristic for Prussian blue magnets (~20 K). Photoinduced effects in  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  were studied by both magnetic and optical spectroscopy methods. The optical studies revealed that PIM in this material is accompanied by changes in the electronic configuration as well as structural changes, which allowed us to determine that the PIM occurs via an entirely novel physical mechanism different from that operating the Prussian blue magnets.

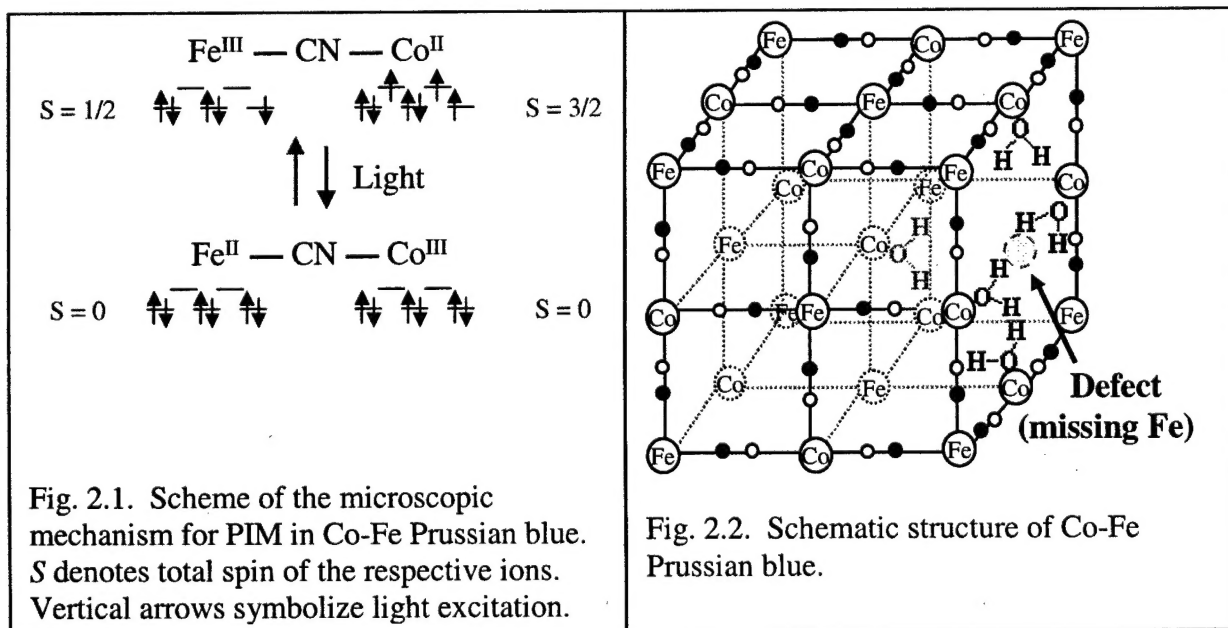
Our studies to date have resulted in several major and well-cited publications in international journals and more than a dozen invited and contributed presentations at

international conferences on physics, chemistry, and materials science. The discovery of PIM in  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  received a notable attention in the broad scientific community and it presents one of the more publicized scientific advances in the first half of 2002 (see Section IV for a list of citations of this discovery).

A summary of our achievements during the previous AFOSR grant (F49620-00-0050) is below.

### Progress and Accomplishments During the Period of the Previous AFOSR Grant No. F49620-00-0050

The completed grant period (1 December 1999 – 30 November 2001) has been one of exciting and rapid progress in our investigations of the phenomenon of photoinduced magnetism. Our research has resulted in a number of major publications (Appendix A.I), invited (Appendix A.II) and contributed (Appendix A.III) talks. It has received a notable recognition from the scientific community, with more than thirty citations in less than two years, as well as attention of a wider audience, reflected in numerous popular articles featuring our work (Section A.IV). A list of publications, presentations, and articles in popular press that have resulted from the studies



under the previous AFOSR grant is presented in Appendix A.

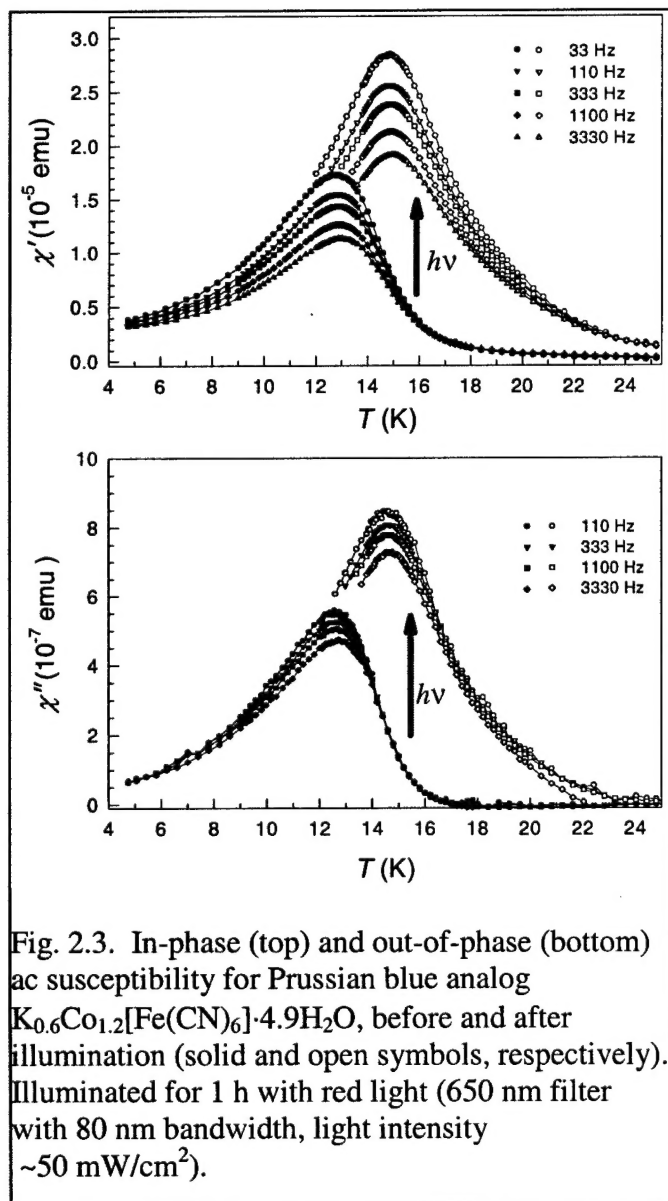
### **Progress in studies of PIM in Co-Fe Prussian blue analogs**

In 1996 fascinating photoinduced magnetic phenomena were reported in cobalt-iron Prussian blue analogs [3]. Depending on stoichiometry, these materials are paramagnets or exhibit long range magnetic ordering at low temperatures ( $< 25$  K). Upon illumination with light in the red region of spectrum dramatic changes in the magnetic state of the materials are observed, including increased magnetic ordering temperature, magnetization, remanence and coercivity [3]. At low temperatures these effects are preserved for several days after illumination. The materials can be brought to the ground state by blue or infrared light excitation, or by warming to  $\sim 150$  K [3, 7]. It has been determined that the mechanism responsible for optically controlled magnetic order is photoinduced inter-ionic electron transfer accompanied by a spin flip, resulting in the increased number of unpaired spins on the metal sites (Fig. 2.1) [3, 8]. It has also been found that the structural disorder, produced by vacancies in  $\text{Fe}(\text{CN})_6$  sites (Fig. 2.2), plays the key role in stabilizing the photoexcited state [7, 9, 10]. The cobalt sites in the vicinity of such a vacancy have reduced ligand field strength, which favors high-spin state  $\text{Co}^{\text{II}}(S = 3/2)$  and allows for easier photoinduced transition from low-spin to high-spin state [7, 11, 12].

While the microscopic origin for PIM has been the subject of extensive studies since the discovery of the effect, the mechanism of magnetic ordering and, particularly, the question whether structural disorder affects the magnetic ordering, were prior to our work not discussed. We performed the first systematic study of the magnetic state in this class of materials, employing both the static and dynamic magnetic susceptibility measurements [13, 14]. The study included detailed analysis of the effects of illumination on virtually every aspect of the magnetic ordering. These studies revealed that the materials exhibit a highly non-conventional type of magnetic ordering. True long-range ferrimagnetic order, assumed in earlier studies, does not occur in these cobalt-iron Prussian blue analogs. Its absence is attributed to a significant

structural disorder noted above. Instead, the materials show a complex low-temperature magnetic behavior with coexisting short-range collinear order and spin glass properties [13, 14]. Our proposed cluster glass model qualitatively level accounts for all the observed magnetic and PIM behavior. In this model the increased spin concentration in the photoexcited state leads to a shift of the entire dynamics of magnetic ordering towards longer length and time scales.

Our breakthrough in understanding the nature of magnetic ordering and the effects of illumination on this ordering was made possible by application of a novel experimental technique. We reported the first use of ac magnetic susceptibility to study PIM [14] in any



material. This was achieved by designing a fiber optics accessible sample holder for our ac susceptometer. This technique ('photo-susceptometry') allows detection of very small light-induced changes in susceptibility ( $\sim 10^{-8}$  emu) and direct observation of changes in spin dynamics produced by the photoinduced transitions.

The data in Figure 2.3 demonstrates application of the photo-susceptometry technique to Co-Fe Prussian blue analog  $K_{0.6}Co_{1.2}[Fe(CN)_6] \cdot 4.9H_2O$ . Both the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) components of the linear ac susceptibility  $\chi_{ac}$  ( $\chi_{ac} = \chi' - i\chi''$ ) were measured in a wide range of frequencies  $f$  of applied ac magnetic field ( $33 \leq f \leq 3300$  Hz). For the state before illumination (ground state), below  $\sim 16$  K the in-phase

component becomes  $f$ -dependent. This is accompanied by occurrence of a nonzero out-of-phase component. At lower temperatures  $\chi'(T)$  and  $\chi''(T)$  exhibit  $f$ -dependent peaks. Frequency dependence of  $\chi_{ac}(T)$  is an evidence for long relaxation times in the system, not observed in systems with conventional long-range magnetic order. The  $\chi'$  peak temperature  $T_p$  has a small relative shift per decade of frequency:

$$\delta T_p \equiv (\Delta T_p / T_p) / \Delta(\log f) \sim 0.01.$$

This fact indicates that magnetic moments in the system undergo cooperative (spin glass-like) freezing, in contrast to progressive blocking of individual moments (superparamagnet-like), for which  $\delta T_p$  is an order of magnitude larger, typically  $\sim 0.5$  [15].

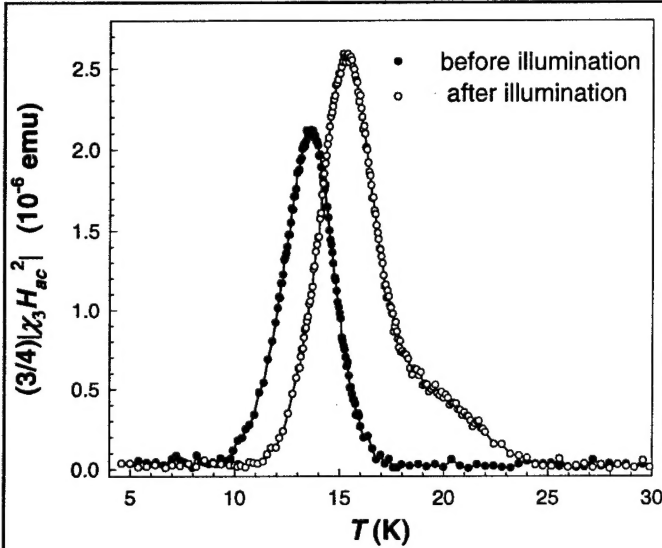


Fig. 2.4. Temperature dependence of the nonlinear susceptibility of  $\text{K}_{0.6}\text{Co}_{1.2}[\text{Fe}(\text{CN})_6] \cdot 4.9\text{H}_2\text{O}$ , before and after 1 h of illumination with red light, measured at frequency of 333 Hz and ac magnetic field of 15 Oe.

In the photoexcited state both components of the ac susceptibility are substantially increased. The susceptibility peak temperatures are increased by  $\sim 2$  K, while the temperature of the onset of

frequency dependence of  $\chi'$  is increased by  $\sim 7$  K. The ac susceptometry method allows for a direct detection of the changes in spin dynamics upon illumination. In the ground state  $\chi'$  in the region  $\sim 16 - 22$  K does not show frequency dependence, indicating that all relaxation times in the system are much shorter than the experimental time window (equal to the inverse frequency, i.e., 30 ms - 0.3 ms). However, in the same temperature region the photoexcited state  $\chi'$  shows pronounced frequency dependence, indicating that the longest relaxation times in the system extend beyond the experimental time window. Thus through photo-ac-susceptometry we directly observe *slowing down of the spin dynamics upon illumination*.



The ac susceptometry also allows for the nonlinear terms in the magnetic susceptibility to be extracted. In general, magnetization ( $M$ ) of any material can be expanded into a sum of powers of the magnetic field  $H$  as

$$M = M_0 + \chi_1 H + a_2 \chi_2 H^2 + a_3 \chi_3 H^3 + \dots,$$

where  $M_0$  is spontaneous magnetization,  $\chi_1$  linear susceptibility and  $\chi_n$  ( $n = 2, 3, 4, \dots$ ) nonlinear susceptibilities [15]. It can be shown that the terms  $\chi_n$  can be determined by detecting the ac susceptibility response by lock-in amplifier at multiples of the frequency  $f$  of the driving magnetic field, as long as the magnitude of the field  $H$  is small [15]. The nonlinear susceptibility  $\chi_3$ , determined by detecting signal at frequency  $3f$ , for both the ground and photoexcited states of  $\text{K}_{0.6}\text{Co}_{1.2}[\text{Fe}(\text{CN})_6] \cdot 4.9\text{H}_2\text{O}$ , is shown in Figure 2.4. In both states  $\chi_3$  exhibits sharp peaks, suggesting divergence of this quantity, as expected for spin-glass type of transition [15, 16]. This result is an additional indication of cooperative freezing of spins in Co-Fe Prussian blue; in contrast, systems with progressive blocking of magnetic moments  $\chi_3$  only show a weak temperature dependence [17, 18]. After illumination  $\chi_3$  is increased and the peak shifts to higher temperature by  $\sim 2$  K. While  $\chi_3$  in the ground state shows a single sharp peak, in the photoexcited

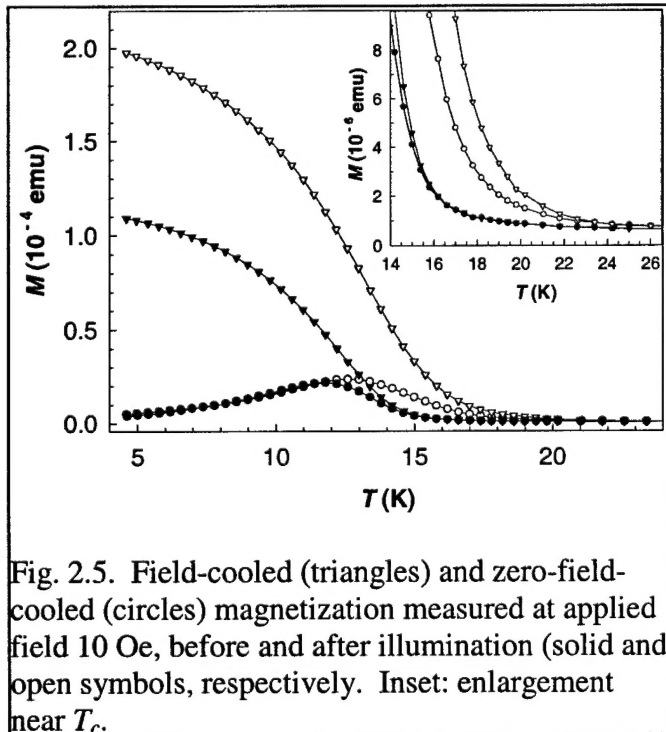


Fig. 2.5. Field-cooled (triangles) and zero-field-cooled (circles) magnetization measured at applied field 10 Oe, before and after illumination (solid and open symbols, respectively). Inset: enlargement near  $T_c$ .

state the peak is overlapped with a weaker, broad feature that extends to  $T \sim 23$  K. We attributed this feature to the response of spin clusters formed by illumination that remain decoupled from the cluster-glass matrix [19].

The ac susceptibility studies were complemented by the detailed studies of the magnetic and PIM response by SQUID dc magnetometry. The temperature dependence of the dc magnetization ( $M$ ) of



$\text{K}_{0.6}\text{Co}_{1.2}[\text{Fe}(\text{CN})_6] \cdot 4.9\text{H}_2\text{O}$ , measured at applied magnetic field  $H = 10$  Oe, is displayed in Fig. 2.5. Below  $T_c \approx 16$  K (for the ground state),  $M$  starts to rapidly increase. At a bifurcation temperature,  $T_b$ , just below  $T_c$ , a deviation between the field-cooled ( $M_{fc}$ ) and zero-field-cooled ( $M_{zfc}$ ) magnetization curves arises, indicating irreversible magnetic behavior. While  $M_{fc}$  increases monotonically as temperature is lowered,  $M_{zfc}$  exhibits a maximum at temperature  $T_{max} \approx 12$  K (in the ground state), below which temperature the irreversibility becomes much more pronounced.

While at low applied magnetic fields the temperature of the  $M_{fc}/M_{zfc}$  bifurcation  $T_b$  approaches  $T_c$ , as  $H$  is increased  $T_b$  shifts to lower temperatures (Fig. 2.6). The presence of

irreversibility, with a field-dependent bifurcation, is characteristic for spin glasses and spin glass-like materials [15, 20].

In the photoexcited state all characteristic temperatures ( $T_c$ ,  $T_b$ , and  $T_{max}$ ) are increased, indicating a shift of the entire dynamics of magnetic ordering to higher temperatures. The field-cooled magnetization at low magnetic fields is almost doubled by illumination (Fig. 2.5).

We detected very slow relaxation of  $M_{zfc}$  and of the thermoremanent magnetization (TRM, measured after cooling in field and subsequently reducing the field to zero) at  $T < T_c$ , which are further indications of long relaxation times in the material, characteristic for a system that undergoes freezing of magnetic moments.

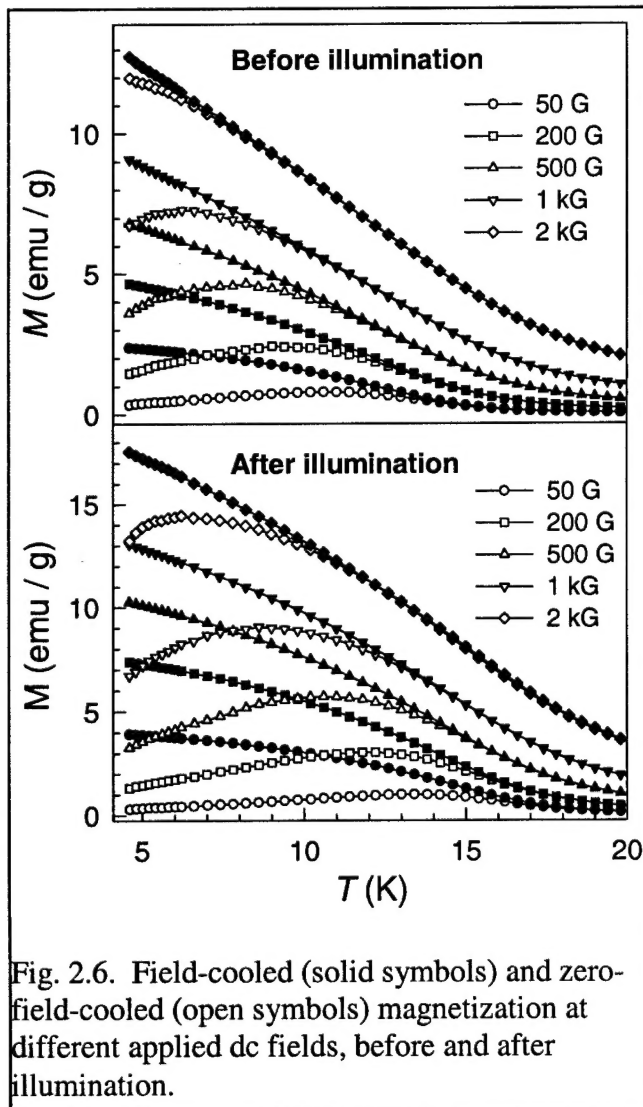
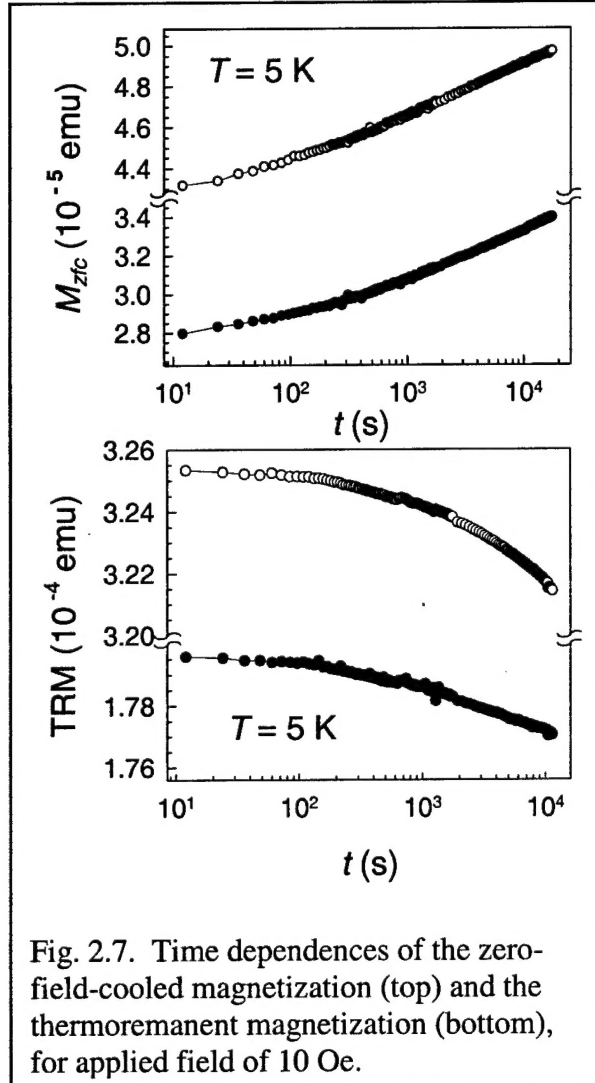


Fig. 2.6. Field-cooled (solid symbols) and zero-field-cooled (open symbols) magnetization at different applied dc fields, before and after illumination.

The time dependences of  $M_{zfc}$  and TRM are displayed in Fig. 2.7.



Based on our experiments, we proposed a model for the magnetic behavior of Co-Fe Prussian blue analogs, as well as for the photoinduced effects on this behavior [14]. The strong irreversibility, the  $f$ -dependent  $\chi_{ac}(T)$  with small values of  $\delta T_p$ , and the slow relaxation of TRM and  $M_{zfc}$  indicate long relaxation times, in contrast to magnetic response of a long-range magnetically ordered system, and suggestive of a spin-glass like magnetic order. However, the monotonic increase in  $M_{fc}$  with decreased  $T$  indicates that short-range collinear order coexists with the spin glass-like order. These facts classify this material as a cluster glass-a system with short-range collinear (ferrimagnetic in this case) magnetic order within spin clusters, and with spin glass-like order among clusters' magnetic moments [14]. The low- $T$  magnetic

response is characterized by two transitions:

(1) At  $T = T_c$  (the 'quasicritical temperature') spin-spin interactions become significant enough to bring about short-range ferrimagnetic ordering of magnetic moments. The transition is characterized by: (i) rapid increase in  $M$ ; (ii) onset of the weak  $M_{fc}/M_{zfc}$  irreversibility; (iii) occurrence of nonzero  $\chi''(T)$ ; (iv) onset of the frequency dependence of  $\chi'(T)$ ; (v) occurrence of the nonlinear susceptibility. We proposed that the ferrimagnetic order is limited to clusters of spins, the sizes of which increase as temperature is decreased, but always remain finite. At temperatures just below  $T_c$  individual clusters undergo progressive blocking due to energy

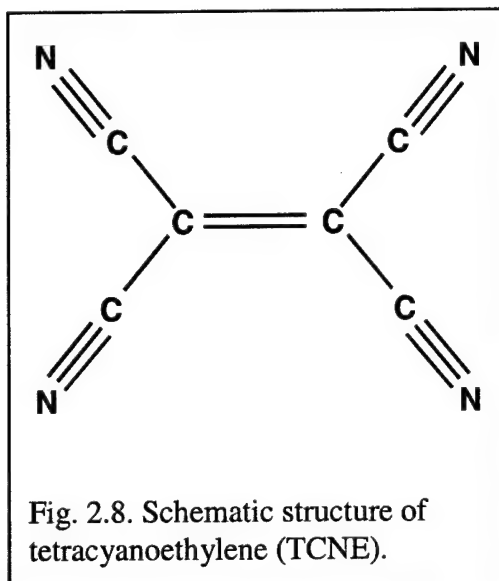
barriers induced by crystalline and shape anisotropies, causing weak irreversibility and frequency-dependent behavior.

(2) At a temperature defined as  $T_f \equiv T_p(f \rightarrow 0)$  (the freezing temperature) the cluster-cluster interactions produce cooperative freezing of their magnetic moments in random directions. The transition is characterized by: (i) peaks in  $\chi'(T)$ ,  $\chi''(T)$  and the nonlinear susceptibility and (ii) onset of the strong  $M_{fc}/M_{zfc}$  irreversibility and a peak in the low-field  $M_{zfc}$ . This process is a real thermodynamic transition (with divergent spin glass correlation length [16]), as suggested by the size of  $\delta T_p$  and divergent-like behavior of the nonlinear susceptibility.

This qualitative model readily incorporates effects of light excitation on the low- $T$  magnetic behavior [13, 14]. Upon light irradiation new spins are introduced into the lattice, as discussed in the introduction. Higher spin concentration ( $n_s$ ) in the photoexcited state enables formation of the spin clusters at a higher temperature  $T_c^{illum.} > T_c$ . Furthermore, at a given temperature, higher  $n_s$  leads to an increase in both the sizes of existing clusters and their magnetization. As larger clusters have longer relaxation times, the entire dynamics of the system is expected to shift to longer length and time scales in the photoexcited state, thus leading to freezing at a higher temperature  $T_f^{illum.} > T_f$ .

We synthesized several Prussian blue analogs  $K_{1-2x}Co_{1+x}[Fe(CN)_6] \cdot yH_2O$ , with  $x$  in the range 0.2-0.4, and detected cluster glass behavior in all these materials [14]. Our studies present the first example of a system with coexisting cluster-glass and PIM behavior, and show that disorder in these materials not only stabilizes PIM but also produces a highly unconventional type of magnetic ordering, a result significant for optimization of the materials for possible applications.

### Discovery and investigations of PIM in the organic-based magnet $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$



The recently synthesized molecule-based magnets  $\text{M}(\text{TCNE})_x \cdot y(\text{solvent})$  ( $\text{M} = \text{V}, \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$ ; TCNE = tetracyanoethylene) are of considerable interest because of their unusual magnetic properties and high magnetic ordering temperatures [5, 6, 21]. In each case the unpaired electrons are on both the manganese ion and the bridging organic ligand  $[\text{TCNE}]^-$  (Fig. 2.8) [21]. The  $\text{M} = \text{V}$  material is one of only a few room-temperature molecule-based magnets [6]. Elaborate magnetic studies and critical analyses

done by our group showed that  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  exhibits paramagnet-ferrimagnet transition at  $T_c = 75 \text{ K}$ , and a reentrant transition to spin glass-like state at temperatures below 10 K [22].

We discovered dramatic PIM effects in  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  ( $x \sim 0.8$ ) upon excitation with light in the blue region of spectrum [23, 24]. While many phenomenological aspects of the PIM are similar to the PIM effect in Co-Fe Prussian blue magnets, detailed analysis strongly suggests a different underlying physical mechanism. This is the first observation of PIM in an organic-based magnet, i.e., magnet with spins that reside on organic species ( $[\text{TCNE}]^-$ ). PIM is observed at temperatures close to the boiling temperature of the inexpensive coolant liquid nitrogen, which is a significant step towards possible applications. A clear goal of the proposed research program is to develop systems where PIM occurs at room temperature.

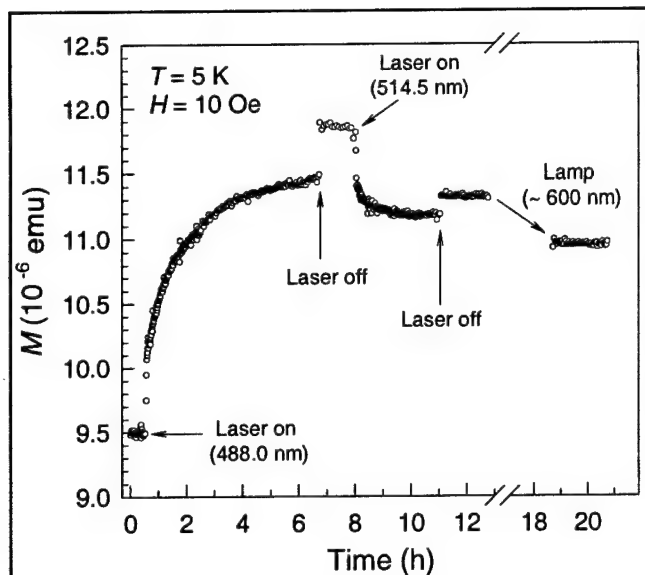


Fig. 2.9. Effects of light excitation on the field-cooled magnetization of  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  ( $x \sim 0.8$ ). Illuminated with argon-ion laser (light intensity  $I \sim 10 \text{ mW/cm}^2$  for both laser lines) and halogen lamp (600 nm filter with 80 nm bandwidth,  $I \sim 10 \text{ mW/cm}^2$ ).

Figure 2.9 shows the effect of illumination on the field-cooled magnetization, measured at  $T = 5 \text{ K}$ , in static magnetic field  $H = 10 \text{ Oe}$ . Upon excitation with 2.54 eV (488 nm) argon laser line, the magnetization increases, and reaches saturation in about six hours. After turning the laser off,  $M$  exhibits an additional increase, Fig. 2.9, due to cooling of the sample ( $M$  decreases with the increase of temperature). The photoexcited state persists even in the dark after illumination. At  $T = 5 \text{ K}$ , the magnetization decreases by only about 0.5% within 60 h

after illumination. Assuming that relaxation of PIM is exponential, this gives a lifetime of the photoexcited state greater than  $10^6 \text{ s}$ . Illumination with 2.41 eV (514.5 nm) laser line leads to a partial reduction of the PIM (Fig. 1). Detailed study shows that PIM nearly identical to the one obtained by the 2.54 eV line can be induced by excitation anywhere in the region  $\sim 2.54\text{--}3.00 \text{ eV}$ , with both monochromatic and broad-band light. A weaker PIM effect is obtained by laser excitation in the region  $\sim 2.35\text{--}2.50 \text{ eV}$ . Partial reduction of PIM is obtained by excitation in the region  $\sim 1.8\text{--}2.5 \text{ eV}$ ; the energies around 2 eV ( $\sim 600 \text{ nm}$ ) are the most effective and reduce PIM to about 60% of its maximum value (Fig. 2.9).

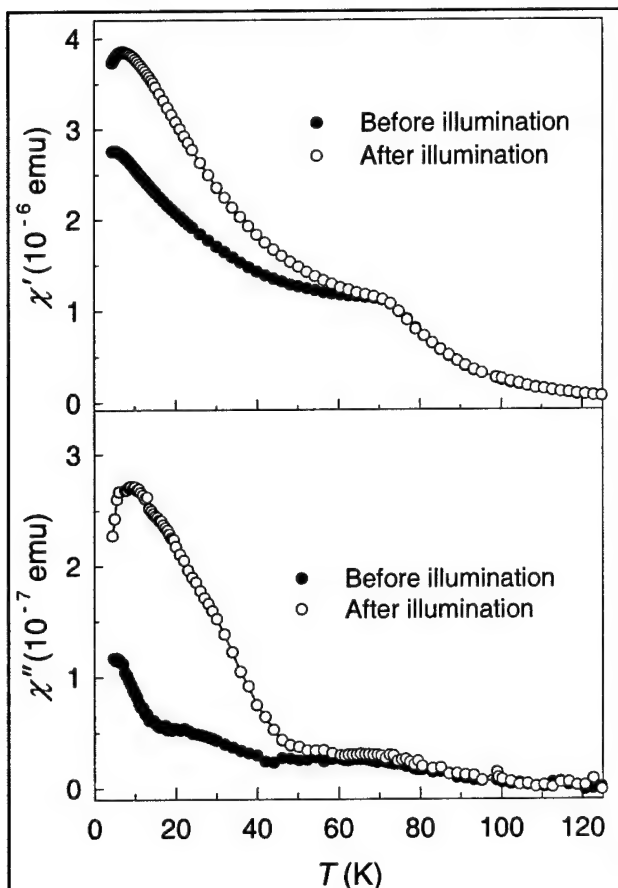


Fig. 2.10. In-phase (top) and out-of-phase (bottom) ac susceptibility of the organic-based magnet  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  ( $x \sim 0.8$ ), before and after illumination, measured at frequency of 333 Hz and applied ac magnetic field of 15 Oe.

The ac susceptibility, for both the ground and photoexcited states, is displayed in Fig. 2.10. The susceptibility shows a shoulder near  $T_c$  (75 K), and a low-temperature peak (at  $\sim 5$  K in the ground state) attributed to the reentrant transition, similar to the previous report [22]. After illumination (argon laser, 2.7 eV line, light intensity  $I \sim 50$   $\text{mW}/\text{cm}^2$ , illuminated at  $T = 90$  K for 60 h,  $\chi_{ac}$  exhibits a large increase in the whole temperature region below  $T_c$ . The low-temperature peak is shifted to  $\sim 7$  K, indicating increased reentrant transition temperature. Enhancement of  $\chi'$  is more than 50% in the region 13-18 K, while increase in  $\chi''$  is more than fourfold in the same temperature region. As the out-of phase component  $\chi''$  is proportional to the area of the hysteresis loop formed during one period of oscillation of the

ac magnetic field [23,25], which is equal to the electromagnetic energy absorbed in the sample, the enhanced  $\chi''$  indicates increased electromagnetic absorption. While the PIM detected below  $T_c$  was obtained by excitation at  $T = 90$  K  $> T_c$ , no PIM was detected in the paramagnetic region ( $T > T_c$ ). This suggests that no new spins are introduced into the system by illumination, which is in stark contrast to the PIM effect in Prussian blue analogs, and suggests a different physical origin of PIM.

The photoexcited state is not fully erased even after warming to 200 K (about 5% of increase in  $\chi'$  is maintained at 5 K). After warming above 250 K the material fully relaxes to

the state before illumination. Thus, while photoinduced effects on the magnetic state were not detected in direct measurement of  $\chi_{ac}$  above  $T_c$ , the photoexcited state is preserved at temperatures high above the magnetic ordering temperature.

In order to determine changes in electronic configuration that accompany the PIM effect, we performed photoinduced absorption (PA) studies in the UV/Visible region of spectrum. The direct absorption spectrum, measured at  $T = 13$  K, is shown in Fig. 2.11(a). The band in the region 2.5-3.5 eV, with pronounced vibrational structure, is assigned to the ( $\pi - \pi^*$  transition of

the  $[\text{TCNE}]^-$  ion, while, the weaker absorption band in the region 1.5-2.5 eV is tentatively assigned to a charge transfer transition between metal and ligand [23]. The spectrum indicates that PIM is obtained by excitation in the ( $\pi - \pi^*$  band, while reduction of PIM is obtained by excitation in the energy region overlapping with the charge transfer band.

The PA spectrum, Fig. 2.11(b), was measured after 10 min illumination with 2.54 eV laser line. The spectrum was obtained by subtracting the direct absorption spectra before and after illumination. Photoinduced absorption is detected in the regions 1.5-2.4 eV and 3.1-3.8 eV, while in the region 2.4-3 eV bleaching (decreased absorption) is observed. These photoinduced effects are also maintained long after illumination, and

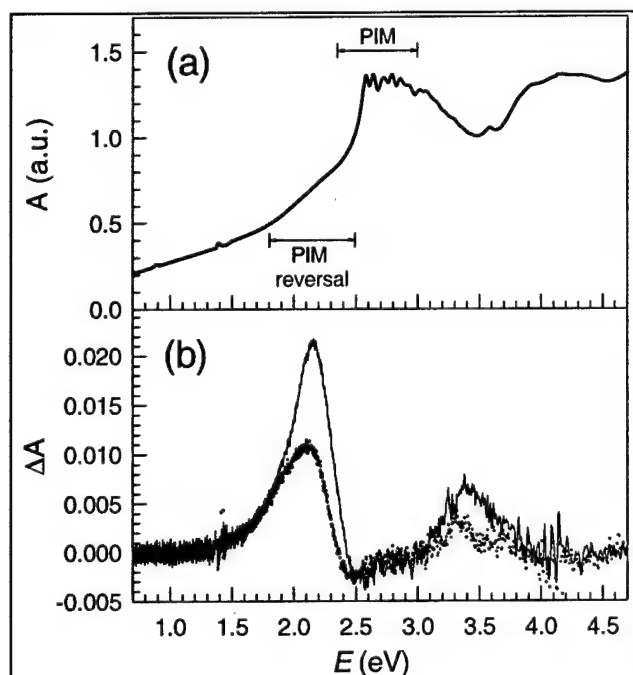


Fig. 2.11. (a) Direct absorption spectrum of  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  ( $x \sim 0.8$ ) at 13 K. The intervals designate regions of excitation energies for which PIM and partial reversal of PIM are observed. (b) Photoinduced absorption spectrum at 13 K.  $\Delta A$  was measured after excitation with 2.54 eV argon laser line (solid line), and after subsequent illumination with 2.41 eV laser line (dots). Light intensity  $\sim 10 \text{ mW/cm}^2$ , 10 min illumination for both laser lines.



can be partially reduced with 2.4 eV line excitation [Fig. 2.11(b)].

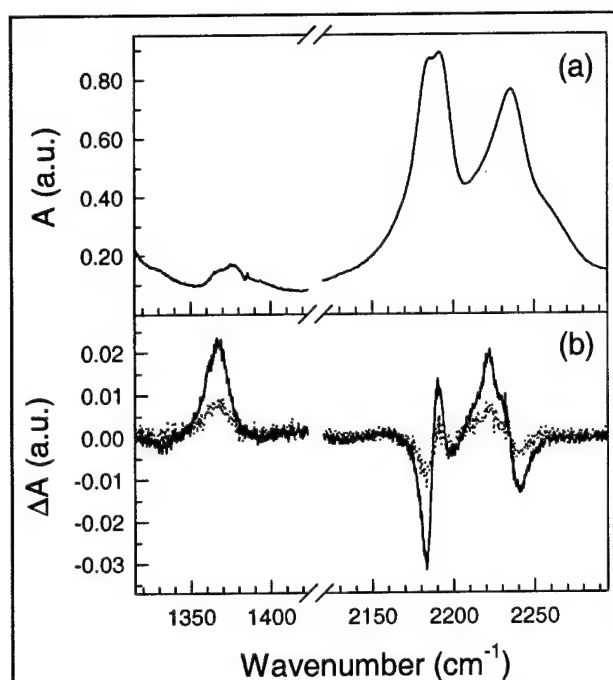


Fig. 2.12. (a) Infrared spectrum measured at 13 K. (b) Infrared photoinduced absorption after illumination with 2.54 eV laser line (solid line), and after subsequent illumination with 2.41 eV line (dots). Light intensity  $\sim 10$  mW/cm<sup>2</sup>, 10 min illumination for both laser lines.

The fact that PIM is induced by the internal  $\pi - \pi^*$  transition of [TCNE]<sup>-</sup> is additional indication that PIM in Mn(TCNE)<sub>2</sub>·x(CH<sub>2</sub>Cl<sub>2</sub>) the ones previously reported. It contrasts the effects observed in Prussian blue magnets, in which excitation of charge transfer bands is responsible for PIM [3], as well as the photoinduced transition between the localized low-spin and high-spin states of metal ions in spin crossover complexes, which is due to the photoinduced internal d-d transitions [26].

The UV-Vis PA, maintained long after illumination, suggests that PIM is due to a photoinduced electronic transition into a long-living (metastable) state. Assuming the

assignment of optical transitions given above, the photoinduced absorption peak at  $\sim 2$  eV, in the region of charge transfer band, indicates that in the metastable state charge transfer is enhanced.

An important question is whether PIM is accompanied by structural changes, i.e., by distorted chemical bonds and/or angles between bonds ('lattice distortions'). Such changes are reflected in the infrared spectrum as alterations of energies and intensities in vibrational modes. In order to answer this question we performed infrared PA studies.

Figure 2.12(a) shows low-temperature infrared spectrum of Mn(TCNE)<sub>2</sub>·x(CH<sub>2</sub>Cl<sub>2</sub>) ( $x \sim 0.8$ ). The peaks in the region 2180-2260 cm<sup>-1</sup> correspond to the C $\equiv$ N stretching modes of [TCNE]<sup>-</sup>, while the peak at 1370 cm<sup>-1</sup> is assigned to the stretching vibration of the central [TCNE]<sup>-</sup> carbon atoms [23]. The PA spectrum after 10 min excitation with 2.54 eV line is

shown in Fig. 2.12(b). The shown effects correspond to a decrease in the magnitude of the 2185  $\text{cm}^{-1}$  peak, while the 2191  $\text{cm}^{-1}$  peak increases. Furthermore, the peak at 2236  $\text{cm}^{-1}$  is slightly shifted to lower energies. Substantial photoinduced absorption also is detected in the region of the 1370  $\text{cm}^{-1}$  mode. Metastability of the photoexcited state and partial reduction of the photoinduced effect by the 2.4 eV line also were observed, Fig. 2.12(b), in full correlation with the effects observed in the magnetic and UV/Vis PA experiments.

As noted above, the changes in the infrared spectrum suggest presence of a structural distortion. Following the optically induced  $\pi \rightarrow \pi^*$  transition, a fraction of electrons may relax from the  $\pi^*$  level into this state with altered geometry, occurring through the electron-phonon coupling. The altered geometry is expected to affect the overlap integrals between the metal and the ligand orbitals, including the spin carrying orbitals ( $d$  orbitals of  $\text{Mn}^{\text{II}}$  and  $\pi^*$  orbitals of  $[\text{TCNE}]^-$ ). As the overlap integrals control both the charge transfer between the metal and coordinating  $[\text{TCNE}]^-$ , and the exchange interaction, both the charge transfer and exchange may be enhanced in the metastable state. This would lead to increased charge transfer absorption and increased magnetic susceptibility, as detected in our experiments.

We proposed [23] that the remarkable metastability of the photoexcited state also has its origin in this lattice distortion. Lattice relaxation may produce a local energy minimum for the excited state, separating it from the ground state by an energy barrier. At low temperatures vibrational excitations are insufficient to surmount the energy barrier, and the system is trapped in the excited state. A lattice distortion was likewise proposed as a key for stabilization of PIM in the case of Prussian blue magnets [7, 11].

These results demonstrate striking effects of visible light on the magnetic, electronic, and vibrational properties of the organic-based magnet  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$ . The high-temperature PIM in an organic-based system, the properties of which are modifiable through versatile organic chemistry methods, opens a promising new pathway towards materials with desired PIM properties.

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## **APPENDIX A**

## I. Publications Citing AFOSR Support

1. D.A. Pejakovic, J.L. Manson, J.S. Miller, and A.J. Epstein, *Cluster Glass State and Photoinduced Effects on the Freezing Dynamics in  $K_xCo[Fe(CN)_6]_y \cdot zH_2O$  ( $x \approx 0.16$ ,  $y \approx 0.72$ ,  $z \approx 4.4$ )*, **Journal of Applied Physics** **87**, 6028-6030 (2000).
2. D.A. Pejakovic, J.L. Manson, J.S. Miller, and A.J. Epstein, *Photoinduced Magnetism, Dynamics, and Cluster Glass Behavior of a Molecule-Based Magnet*, **Physical Review Letters** **85**, 1994-1997 (2000).
3. J.S. Miller and A.J. Epstein, *Molecule-based Magnets – An Overview*, **Materials Research Society Bulletin** **25** (11), 21-28 (2000).
4. A.J. Epstein, *New Phenomena and Opportunities in Molecule-based Magnets*, **Materials Research Society Bulletin** **25** (11), 33-40 (2000).
5. D.A. Pejakovic, J.L. Manson, J.S. Miller, and A.J. Epstein, *Manipulating Magnets with Light: Photoinduced Magnetism in Cobalt-Iron Prussian Blue Analogs*, **Current Applied Physics** **1**, 15-20 (2001).
6. D.A. Pejakovic, J.L. Manson, J.S. Miller, and A.J. Epstein, *Photoinduced Magnetism in a Cluster Glass: Co-Fe Prussian Blue*, **Synthetic Metals** **122**, 529-533 (2001).
7. D.A. Pejakovic, J.L. Manson, C. Kitamura, J.S. Miller, and A.J. Epstein, *Photoinduced Magnetization in Molecule-based Magnets  $K_xCo_y[Fe(CN)_6] \cdot zH_2O$  ( $x \approx 0.31$ ,  $y \approx 0.77$ ,  $z \approx 3.54$ ) and  $Mn(TCNE)_x \cdot y(CH_2Cl_2)$  ( $x \approx 2$ )*, **Polyhedron** **20**, 1435-1439 (2001).
8. D.A. Pejakovic, C. Kitamura, J.S. Miller, and A.J. Epstein, *Optical Control of Magnetic Order in  $Mn(TCNE)_x \cdot y(CH_2Cl_2)$  Molecule-Based Magnet*, **Journal of Applied Physics** **91**, 7176-7178 (2002).
9. D.A. Pejakovic, C. Kitamura, J.S. Miller, and A.J. Epstein, *Photoinduced Magnetization in the Organic-Based Magnet  $Mn(TCNE)_x \cdot y(CH_2Cl_2)$* , **Physical Review Letters** **88**, 057202/1-057202/4 (2002).
10. D.A. Pejakovic, J.L. Manson, C. Kitamura, J.S. Miller, and A.J. Epstein, *Control of Magnetic Order by Light in Molecule-Based Magnets*, **Molecular Crystals, Liquid Crystals** **374**, 289-302 (2002).

## II. Invited Talks Citing AFOSR Support

1. A.J. Epstein, D.A. Pejakovic, J.L. Manson, and J.S. Miller, *Cluster Glass State and Photoinduced effects on the Freezing Dynamics of  $K_xCo[Fe(CN)_6]_y \cdot zH_2O$  ( $x \sim 0.16$ ,  $y \sim 0.72$ ,  $z \sim 44$ )*, **Symposium in Honor of Joel S. Miller Receipt of the ACS Chemistry of Materials Award, 219<sup>th</sup> ACS National Meeting**, San Francisco, CA, 26-30 March 2000.
2. A.J. Epstein, *Molecule-Based Magnets: New Physics and New Opportunities*, **Electronic Structure and Magnetism in Complex Materials**, Washington, DC, 26-28 July 2000.
3. A.J. Epstein, *Photoinduced Magnetism in a Cluster Glass: Co-Fe Prussian Blue*, **VIIIth International Conference on Molecule-Based Magnets**, San Antonio, Texas, September 16-21, 2000.
4. K. I. Pokhodnya, J.S. Miller, D.A. Pejakovic, and A.J. Epstein, *Comparative Study of  $V[TCNE]_x$  Magnet Prepared by Solution Reaction and CVD Technique*, **VIIIth International Conference on Molecule-Based Magnets**, San Antonio, Texas, September 16-21, 2000.
5. J.S. Miller and A.J. Epstein, *Manganoporphyrin-based Magnets*, **2000 International Chemical Congress of Pacific Basin Societies (Pacifichem 2000)**, Honolulu, Hawaii, December 14-19, 2000.
6. A.J. Epstein, D.A. Pejakovic, J.L. Manson, and J.S. Miller, *Photoinduced Magnetism, Dynamics, and Cluster Glass Behavior of Molecule-based Magnets*, **2000 International Chemical Congress of Pacific Basin Societies (Pacifichem 2000)**, Honolulu, Hawaii, December 14-19, 2000.
7. A.J. Epstein, *Organic Based Magnets: New Materials and New Phenomena*, **Sixth International Conference on Frontiers of Polymers and Advanced Materials**, Recife, Brazil, March 4-9, 2001.
8. A.J. Epstein, *Organic-based Magnets, Opportunities in a New Frontier*, **Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications**, Center for Advanced Molecular Materials, Glumslöv, Sweden, June 4-8, 2001.
9. A.J. Epstein, *Organic-based Magnets*, **National Research Council, National Materials Advisory Board, National Research for Defense-After-Next**, J. Erik Jonsson Center, Woods Hole Center of the National Academy of Sciences, Woods Hole, MA, June 26-28, 2001.
10. A.J. Epstein, *Metal/Electronic Interfaces—Impact on LEDs and Corrosion Protection*, **IUPAC/ACS Symposium: MMC-9**, Brooklyn, NY, August 21, 2001.



11. A.J. Epstein, *Photoinduced Magnetism: Using Light to Control Magnetism*, **2002 Gordon Research Conference on Electronic Processes in Organic Materials**, Newport, Rhode Island, July 21-26, 2002.
12. A.J. Epstein, *Organic-based Magnets: New Concepts for Science and Technology*, **New Mountains to Climb: New Phenomena, Materials and Technologies for the 21<sup>st</sup> Century**, *Festschriften Honoring Alan G. MacDiarmid's Achievements for his 75<sup>th</sup> Year*, Dallas, Texas, December 6-7, 2002.
13. A.J. Epstein, *New Physics and Phenomena: From Photoinduced Magnetism to Spintronic Materials*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003.
14. A. J. Epstein, *New Developments in Magnetism from Organic Based Magnets*, **Alvin L. Kwiram Symposium on Optical, Electrical, and Magnetic Properties of Organic and Hybrid Materials**, Seattle, WA, June 23-25, 2003.
15. A.J. Epstein, *Conventional and Unconventional Magnetism in Organic-Based Solids: New Opportunities in New Materials*, **The 2003 Ralph and Helen Oesper Symposium**, University of Cincinnati, October 11, 2003.
16. J.S. Miller, *Organic Magnets: New Chemistry, New Bonding, and New Materials for the New Millennium*, **The 2003 Ralph and Helen Oesper Symposium**, University of Cincinnati, October 11, 2003.
17. A.J. Epstein, *Organic-based Magnets Fractal Behavior, Photoinduced Magnetism, and Spintronics*, **International Conference on Quantum Transport in Synthetic Metals and Quantum Functional Semiconductors**, Seoul, Korea, November 20-22, 2003.

### III. Contributed Talks and Presentations Citing AFOSR Support

1. D.A. Pejakovic, J. Zhang, J.S. Miller, and A.J. Epstein, *Photoinduced Magnetism in  $Mn(TCNE)_2x(CH_2Cl_2)$  High- $T_c$  Molecule-based Magnet*, **VIIth International Conference on Molecule-Based Magnets**, San Antonio, Texas, September 16-21, 2000.
2. A.J. Epstein, *Organic Based Magnets: Old and New Physics in Unfamiliar Materials*, **Seminar, Materials Science Division, Argonne National Laboratory**, Argonne, Illinois, November 15, 2000.
3. A.J. Epstein, *Overview of Organic-Based Magnets*, **Seminar, University of Tokyo, Kamaba Campus**, Tokyo, Japan, October 29, 2001.
4. A.J. Epstein, *Unusual Phenomena in Organic-Based Magnets, Photoinduced Magnetism and Magnetic Organic Semiconductors*, **Seminar, University of Tokyo, Kamaba Campus**, Tokyo, Japan, October 30, 2001.
5. A.J. Epstein, *Organic-Based Magnets: A New Frontier for Physics, Chemistry and Technology*, **Seminar, Waseda University**, Tokyo, Japan, October 31, 2001.
6. A.J. Epstein, *Organic-Based Magnets: A New Frontier for Physics and Chemistry*, **Seminar, Tokyo Metropolitan University**, Tokyo, Japan, November 2, 2001.
7. A.J. Epstein, *Organic-Based Magnets: A New Frontier for Physics*, **Seminar, Department of Physics, Kyoto University**, Kyoto, Japan, November 5, 2001.
8. A.J. Epstein, *Organic-Based Magnets: A New Frontier for Chemistry, Physics and Technology*, **Seminar, Department of Physics, Osaka University**, Osaka, Japan, November 6, 2001.
9. D.A. Pejakovic, A.J. Epstein, C. Kitamura, J. Raebiger, and J. S. Miller, *Metastable States and Photoinduced Magnetization in Organic-Based Magnets  $M(TCNE)_2 \cdot x(CH_2Cl_2)$ ,  $M=Mn, Fe$* , **Meeting of the American Physical Society**, Indianapolis, Indiana, March 18-22, 2002 [Bulletin of the American Physical Society **47**, 722-723 (2002)].
10. A.J. Epstein, *Organic-based Magnets, From an Unknown to Photoinduced Magnetism and Spintronics*, **Colloquium, University of Buffalo at SUNY**, Buffalo, New York, April 25, 2002.
11. A.J. Epstein, *Organic-based Magnets: From Impossibility to Fractal Magnets, Photoinduced Magnetism and Spintronics*, **Colloquium**, The Ohio State University, Columbus, Ohio, January 7, 2003.

12. J.W. Yoo, D.A. Pejakovic, H. Tokoro, S.I. Ohkoshi, K. Hashimoto, and A.J. Epstein, *Magnetic Behavior and Photoinduced Demagnetization in Rubidium Manganese Hexacyanoferrate*, **Meeting of the American Physical Society**, Austin, Texas, March 3-7, 2003 [Bulletin of the American Physical Society 48, 1378 (2003)].
13. A.J. Epstein, *Organic-Based Magnets: From Low and High Temperature Magnets to Photoinduced Magnetism and Spintronics*, **Colloquium, Joint Institute of Chemical Physics**, Moscow, Russia, September 5, 2003.
14. A.J. Epstein, *Organic-Based Magnets: From Discovery to Room Temperature Magnets, Photoinduced Magnetism and Spintronics*, **Colloquium, Ioffe Institute**, Saint Petersburg, Russia, September 9, 2003.
15. A.J. Epstein, *Organic-Based Magnets: From Discovery to Room Temperature Magnets, Photoinduced Magnetism and Spintronics*, **Colloquium, Industrial Technology Research Institute**, Hsinchu, Taiwan, November 4, 2003.

#### IV. Press Articles Citing Research Supported by AFOSR

1. "Researchers Develop World's First Light-Tunable 'Plastic' Magnet," **Ohio State Research News**, February 2002.
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5. "Researchers Develop World's First Light-Tunable 'Plastic' Magnet," **Newswise.com**, February 2, 2002.
6. "Magnet-Kunststoff Wird Durch Laser Eingeschaltet," **Heise Online**, February 2, 2002.
7. "Plastikmagnet ist durch Licht beeinflussbar Kostengünstige Anwendungsmöglichkeit in Computerspeichern," **Frankfurter Allgemeine Sonntagszeitung**, February 3, 2002, NR. 5.
8. "Researchers Develop World's First Light-Tunable 'Plastic' Magnet," **Spacedaily.com**, February 4, 2002.
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10. "First Light-Tunable Plastic Magnet," **The Washington Times**, February 4, 2002.
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13. "Light Activates Magnetic Plastic," **Optics.org**, February 6, 2002.
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43. **Wired News**, *Better PCs with Plastic Magnets*, October 15, 2002, <http://www.wired.com/news/technology/0,1282,55386,00.html>

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